

Heat Loss-Induced Oscillation of Methane and Ethylene in a Perfectly Stirred Reactor

B. Dally¹ and N. Peters²

¹School of Mechanical Engineering
The University of Adelaide, SA, 5005, Australia

²Institute of Combustion Technology,
RWTH Aachen, Aachen 52064, Germany

Abstract

Temperature oscillations for Methane and Ethylene fuel mixtures oxidation at reduced temperatures were calculated using the transient perfectly stirred reactor model. It was found that the oscillations are controlled by the heat loss to the surroundings and are independent of inlet temperatures. Also found that the recombination channel route is not prevalent in lean and stoichiometric mixtures and that there is plenty of evidence that a simple radical scavenging by the fuel is the controlling mechanism.

1 Introduction

Many practical applications employ low temperatures either for a chemical processes [1], in cool flames [2] or through exhaust gas recirculation [3,4,5]. At these conditions temperature oscillation may ensue through two different mechanisms. The first oscillation is caused by thermo-kinetic effects which has been the subject of few studies in the past [1,6,7,8]. While the second naturally occurring oscillations are those found in the combustion of high hydrocarbons where negative temperature gradients have been identified as part of the two stage ignition process [9,10]. This process is purely driven by kinetic effects and is independent of any physical parameters especially heat loss.

At a temperature range of 1000 K to 1300 K and for a variety of equivalence ratios it was found that the oxidation of simple hydrocarbon fuels can go through a cyclic oscillation driven by a combination of heat loss and kinetic effects. De Joannon et al, [6,7] have reported on measurements and modelling of these oscillations for methane oxidation under Jet Stirred Reactor, JSR, conditions. They classified the behaviour of these oscillations, at atmospheric pressure, based on the inlet temperature, C/O ratios and residence time. The range of such behaviour was found to exist at inlet temperatures of 1000K-1300 K, C/O ratios between 0.05 and 0.55 and residence time between 0.35 and 0.5. Using a transient PSR model they reported on the chemistry path which may prevail at different conditions and highlighted the effect of the $C_{(2)}$ species, and in particular the recombination path, on the oscillation. In their work they ignored the effect of heat loss magnitude on these oscillations and seem to have operated at ambient temperatures similar to those at the inlet. As this process is highly affected by heat loss such parameter ought to also be investigated.

Sabia et al[8] extended this work to investigate the effect of hydrogen enrichment. They found that addition of H_2 increased the reactivity of the system and reduced the range where oscillation can occur.

In this paper we examine, computationally, the applicability of the recombination analysis, as a source of the oscillation for lean and stoichiometric conditions of methane fuel mixtures. We also extend this analysis to Ethylene fuel as a mean to identify the driving mechanism of the oscillation.

2 Computational Model

The transient Perfectly Stirred Reactor model of the Chemkin4.1 package was used in this study along with detailed chemical kinetic mechanism (GRI3.0[11]) and a skeletal mechanism (Updated Smooke[12,13]). This zero dimensional model which assumes homogeneous mixture also allows for heat loss from the reactor. The reactor is assumed to be infinitely thin and the linear heat convection equation is used, with constant coefficient, to calculate the heat loss term in the gas energy equation. The reactor size used in this study match that of De Joannon et al [6] which has a volume of 110 cm^3 , an internal surface area of 113 cm^2 and an external surface area of 128 cm^2 . The heat transfer coefficient was fixed at 0.01 cal/cm^2Ks . The pressure was set to 1 atmosphere. For a specific fuel type the C/O ratio, residence time (τ), and inlet and ambient temperatures were investigated. Two fuels were used in this study namely: Methane and Ethylene. Nitrogen was added to the fuel and air mixture in order to keep the temperature inside the reactor at the desired range. In all runs presented here the mole fraction of N_2 was fixed at 85%.

3 Results and Discussion

3.1 Recombination versus Oxidation Path

De Joannon et al, [6,7] argues that at low temperatures, in the range of 1000-1300 K, and at least for methane, the recombination route is more prevalent and the methyl radical CH_3 recombines to form $C_2H_6 \rightarrow C_2H_5 \rightarrow C_2H_4 \rightarrow C_2H_3 \rightarrow C_2H_2$. As acetylene is a relatively stable species, at temperatures higher than 1200K, it is argued that it is expected to dramatically reduce the reactivity of the system and to be responsible for the oscillations. De Joannon et al, [6] also showed that by reducing the activation energy for the recombination reactions the oscillations stopped.

In order to test this observation further we have performed computations using the Transient PSR code for $CH_4/O_2/N_2$ mixtures at conditions similar to those quoted by the above study. The computations were performed using both the GRI 3.0 mechanism as well as the updated Smooke skeletal mechanism, SMK. The latter only contains $C_{(1)}$ species and was used to examine the role of the recombination channel.

Figure 1 shows one cycle of the oscillations using both mechanisms. The top plot shows the SMK results while the bottom plot shows the GRI 3.0 results. The operating conditions are those described in Table 1. It is clear from this figure that oscillation of similar magnitude exist when using both mechanisms. Also apparent is the mechanism which is triggering these oscillations. Here methane consumes all the radicals which are produced at these temperatures until the fuel is fully consumed while at the same time CO and H₂, as intermediates, are being produced.

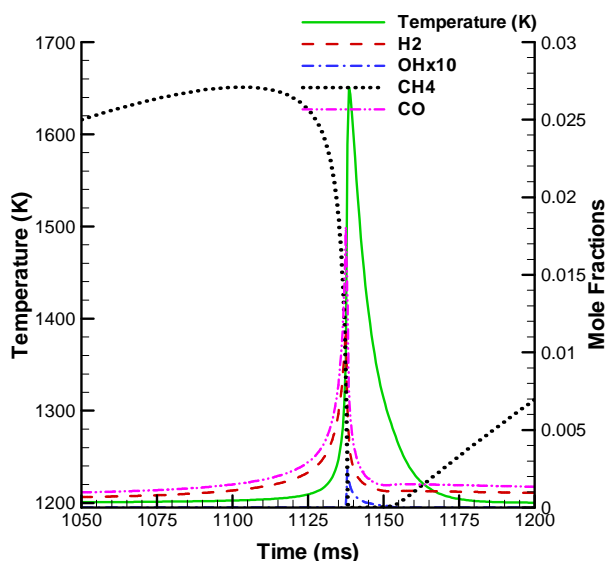
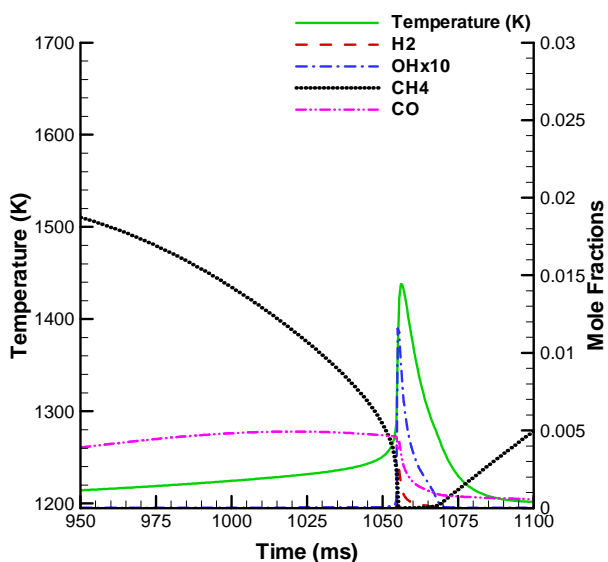


Figure 1 Calculated temperature and species Mole fraction for one cycle using SMK (top) and GRI 3.0 (bottom). Operating conditions as listed in table 1.

The temperature during this process remains low. The fuel totally disappears at 1055 ms for SMK and 1136 ms for GRI 3.0 and at the same time the OH radical increases rapidly and with it the temperature. This increase happens at the same time as CO and H₂ are being consumed. It is well established that the oxidation of these intermediates are responsible for the temperature increase. At the time when maximum temperature is reached there is no source of energy to sustain this temperature and due to the difference with ambient conditions

heat loss to the surroundings is at its maximum. This cause the temperature to drop to its initial conditions and the process repeats itself once there is sufficient fuel in the reactor.

Note worthy is that the difference in the time where the cycle starts for both runs is due to the ignition phenomenon and is not related to the oscillation itself.

Fuel	C/O	τ (s)	T _{in} (K)	T _{amb} (K)
CH ₄	0.25	0.3	1200	1200

Table 1 Operating Conditions for Transient PSR Calculations. C/O is the ratio of carbon to oxygen, τ is the residence time in the reactor, T_{in} is the temperature of the reactants at the inlet and T_{amb} is the surrounds temperature.

Figure 2 shows the C₍₂₎ chain species plotted versus time for the same cycle analysed in Figure 1. It is clear that some recombination takes place during this cycle except that the mole fraction of these species as compared with the other intermediates does not seem to be of significance to cause the oscillations described earlier. In addition the amount of C₂H₂ and that of CH₂CHO is also miniscule to contribute to the oscillation.

Similar runs where also performed using reduced 4 step mechanism and similar oscillation were found. It is hence evident that oscillations are triggered by a simpler mechanism of radical scavenging rather than a recombination channel. This does not however rule out the existence of a recombination route. It just shows that it is not a major contributor to the oscillations. Note worthy, is that we were not able to get any oscillations with C/O>0.25 where excess fuel may activate this recombination channel.

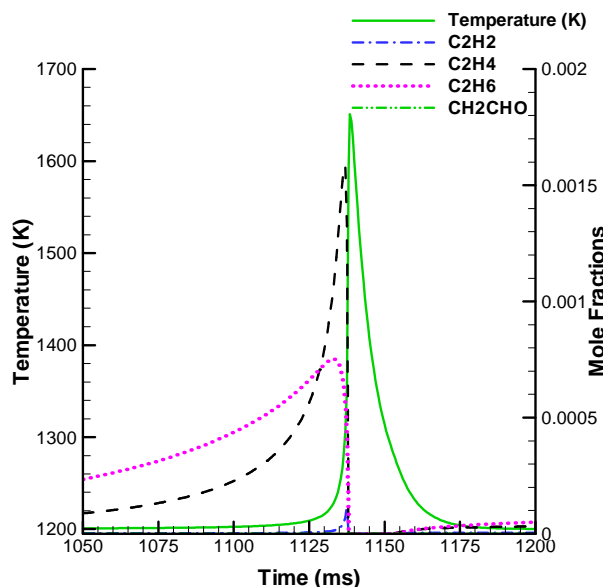


Figure 2 Calculated temperature and mole fraction of C₍₂₎ species plotted against time for the same cycle in Figure 1 using the GRI 3.0 mechanism.

Figure 3 shows the effect of adding C₂H₄ to the fuel mixture while maintaining all operating conditions the same. Here the inlet temperature was set to 300 K, the ambient temperature was 1150 K and C/O ratio is 0.23. The top plot is for pure methane, the middle plot is for an equal volumetric mixture of CH₄ and C₂H₄ while the bottom plot is for pure C₂H₄. It is

clear that there are some differences in the profiles of H_2 and CO while the overall behaviour remained the same. The addition of C_2H_4 is supposed to enhance the recombination channel substantially but no increase in C_2H_2 production was noticed in any of the calculations (not shown).

3.2 Effect of Inlet and Ambient Temperatures

Here we examine the dependency of the oscillations on the inlet and ambient temperatures. The ambient temperature in particular has direct relation to heat loss which is believed to be essential for the oscillations to happen. De Joannon et al, [6,7] reported on conditions where the surrounding temperature was the same as the inlet temperature. They then classified the oscillations using the inlet temperature as a parameter. Our previous observations have shown that heat loss to the surrounding plays an important role in the oscillations. Hence we set out to isolate the effect of the surrounding temperature from that of the inlet temperature. Many runs were performed for different C/O ratios and residence times using the GRI 3.0 mechanism. It was found that the ambient temperature is the dominant parameter that controls the oscillation, consistent with the role of heat loss. Worth noting that the heat transfer coefficient was maintained constant for all computed cases. At the same time it was found that the oscillation is independent of the inlet temperature contrary to previous findings [6,7].

Figure 4 shows the oscillations pattern for three cases with similar operating conditions as those reported in Table 1, except that the inlet temperature was set to 300 K, 750 K and 1200 K. From the figure it is clear that the inlet temperature has little effect on the oscillation pattern and magnitude. It also does not have any influence on the different temperature regimes identified by others [6,7]. For the 300 K and 750 K cases the minimum temperature is slightly lower than the ambient temperature. This is an effect of introducing into the reactor a mixture of reactants at a low temperature. In this case there is a small heat transfer into the reactor, negative heat loss. In fact the heat loss profile versus time is very similar to that of the reactor temperature which further points to the importance of heat transfer on the oscillation.

It is important to note that this independence of the inlet temperature only apply to this case where the residence time is relatively long and mass flow rate of the reactants is small as compared to the thermal mass of the reactor itself. If this ratio changes the inlet temperature may have more influence on the oscillations and temperature response. Such conditions, however, are not dissimilar to those found in a furnace environment.

Figure 5 shows the effects of the ambient temperature on the temperature oscillation for the same cases as above except that the inlet temperature was fixed at 300K. It is clear from this figure that the ambient temperature, and the heat loss, has direct effect on the magnitude and frequency of the oscillations.

4 Conclusions

Transient calculations of a perfectly stirred reactor were performed for methane and ethylene fuels at low temperature conditions in the range of 1000 K to 1300 K. It was found that oscillations are independent of the inlet temperatures and are most controlled by the heat loss from the reactor. Also found that for lean and stoichiometric conditions a simple radical scavenging by the fuel is the prevalent mechanism for the initiation of the oscillations followed by heat loss to the

surrounds. No evidence was found to support the recombination channel route suggested by others.

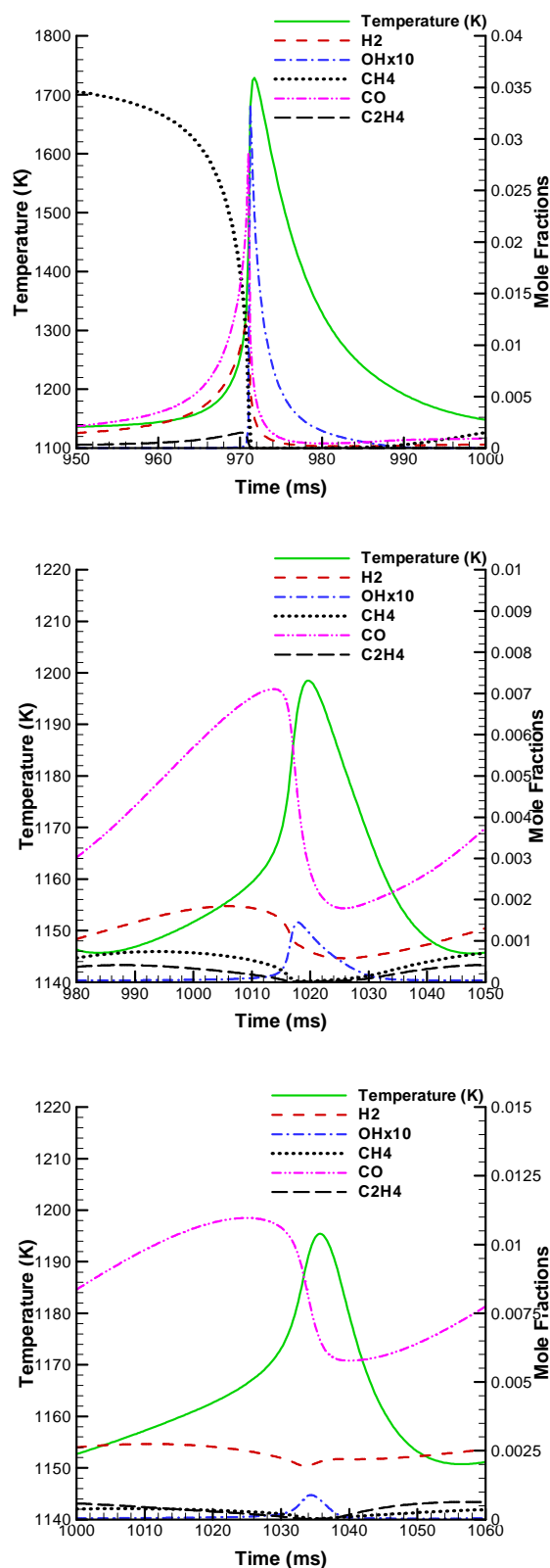


Figure 3 Calculated temperature and mole fractions of species for one cycle using the GRI 3.0 mechanism plotted versus time. Top plot is for pure CH_4 , middle plot for an equal mixture (vol.) of CH_4 and C_2H_4 and the bottom plot for pure C_2H_4 .

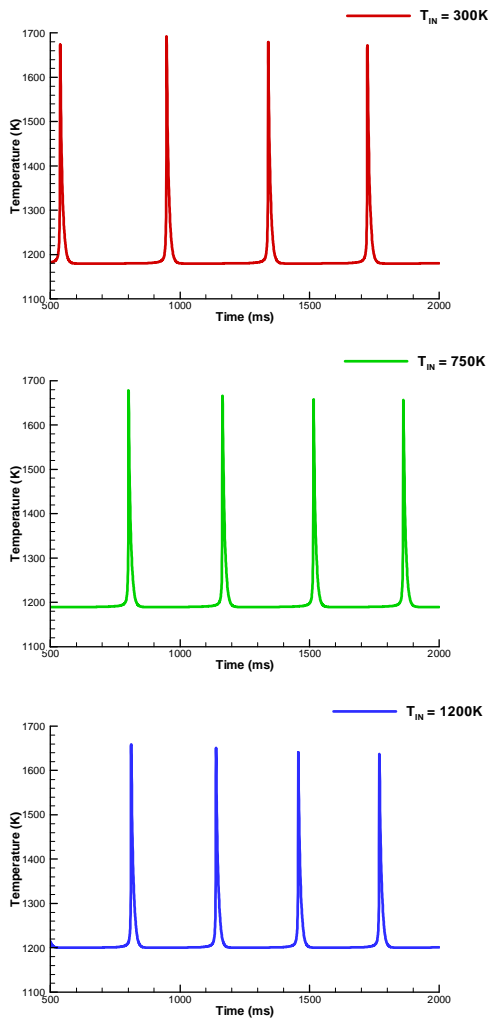


Figure 4 Calculated temperature response versus time for the same conditions as listed in Table 1 except for the different inlet temperatures.

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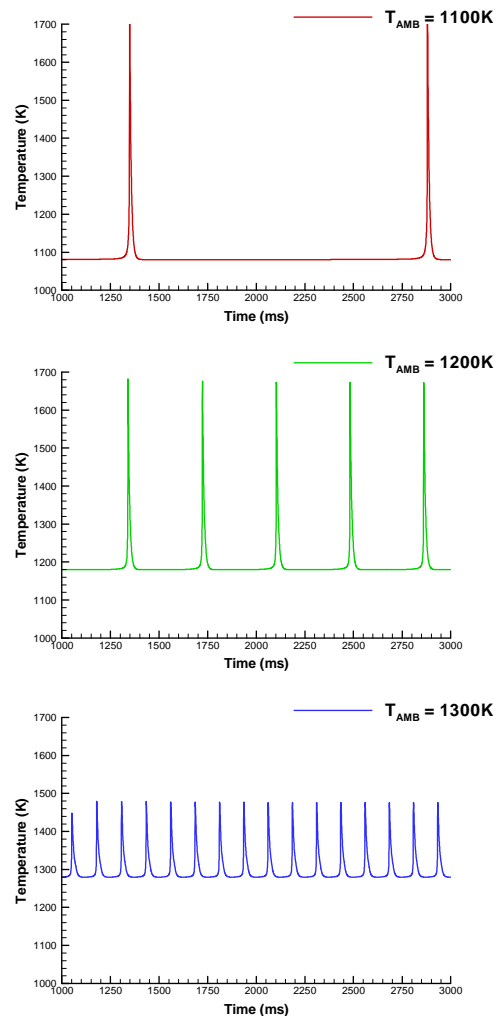


Figure 5 Calculated temperature response versus time for the same conditions listed in Table 1 except with different ambient temperatures and $T_{in}=300K$.

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